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固/固界面的构筑及其电化学性质

Construction of Solid/Solid Interface and Its
Electrochemical Behavior

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Construction of Solid/Solid Interface and Its Electrochemical Behavior

A Dissertation Submitted for the Degree of Master of Science

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摘要

扫描电化学池显微镜 (Scanning Electrochemical Cell Microscopy, 简称 SECCM) 是一种从扫描电化学显微镜 (Scanning Electrochemical Microscopy, 简称 SECM) 基础上发展的新型探针技术, 被广泛用来研究样品表面和界面的电化学、电导、电荷转移、催化活性、形貌等物理化学性质。SECCM 通过拉制的毛细管尖端形成的微液滴, 可以进行高分辨率的电化学测试。为了保证电化学测试的顺利进行, 微液滴内电化学物种浓度不能轻易改变。微液滴由于尺寸小, 一小部分的水蒸发便会导致电解质的浓缩, 容易造成探针的堵塞。而我们利用微液滴容易使电解质析出这一特点, 通过 SECCM 的电化学加工了一系列的功能微晶体, 并将其构筑到微芯片上, 研究了功能微晶体的电化学性质和固/固界面的电荷转移行为。基于 SECCM 的新型微加工技术, 本论文主要研究内容和结果如下。

1. 通过 SECCM 在微芯片上构筑了钴氰化钠/氯化钠固态溶液微晶体, 发现微晶体表现出在水溶液中难以观察到的 Co(III) 的电化学还原现象, 求得 Co(III) 的表观浓度为 $9.69 \times 10^{-2} \text{ mol/L}$, Na^+ 离子在微晶体中的表观扩散系数为 $3.89 \times 10^{-8} \text{ cm}^2/\text{s}$, 固态溶液在金电极上的表观异相电子转移速率常数为 $1.06 \times 10^{-5} \text{ cm/s}$ 。通过密度泛函理论 (DFT), 发现 Co(III) 在 NaCl 晶体中的还原是因为 NaCl 晶体的介电常数小, 降低了 Co(III) 还原的能垒。

2. 应用 SECCM 合成了铁氢氧化物/氯化钠微晶体, 发现了微晶体具有有多步电子转移的固态电化学性质, 利用循环伏安法、计时电位法和电化学阻抗谱表征了微晶体的固态电化学性质, 求得了铁氢氧化物的表观浓度为 $1.55 \times 10^{-2} \text{ mol/L}$, Na^+ 离子在固态溶液的表观扩散系数为 $5.36 \times 10^{-10} \text{ cm}^2/\text{s}$, 固态溶液与金电极界面上的表观异相电子转移速率常数为 $1.29 \times 10^{-4} \text{ cm/s}$, 固态溶液的质量比容量为 625.5 mA h/g 。提出了铁氢氧化物吸附的水分子是微晶体展现电化学性质的重要因素, 揭示了微晶体电化学反应时传质传荷的过程。对微晶体进行高温煅烧, 得到了具有开关性质的半导体铁氧化物, 求得其非线性系数为 1.92。

3. 基于 SECCM 的电化学调制方法原位合成六氯合铈酸二钠/氯化钠固态溶

液。在固态溶液电化学特性研究中发现，溶液经过一个高电位（5V）活化后，电化学特性得到很大的改善。通过 hopping 机理解释了固态溶液的电子转移行为。通过循环伏安技术和电化学阻抗技术，求得了微晶体内 Ir（IV）的表观浓度为 0.46 mol/L，Na⁺离子的表观扩散系数为 $4.46 \times 10^{-9} \text{ cm}^2/\text{s}$ ，微晶体与金微米线的固/固界面表观电子转移速率常数为 $1.14 \times 10^{-4} \text{ cm/s}$ 。

关键词： 扫描电化学池技术； 固态溶液； 构筑； 微加工； 固/固界面

Abstract

Scanning electrochemical cell microscopy(SECCM) is a novel probe technique based on scanning electrochemical microscopy(SECM). It is widely used to measure electrochemical activity, conductance, electron transfer, catalytic activity and topographical visualization of surfaces and interfaces. The meniscus or droplets formed on the pulled micropipette tip allow a high-resolution electrochemical measurements. The concentration of electrochemical species in meniscus should be kept in surroundings with constant humidity to assure a successful electrochemical measurement. Because of the small meniscus dimension, even tiny evaporation of solvent would cause a highly concentrated electrolyte. The concentrated electrolyte easily blocks the micro/nano scaled probe. Thanks to the evaporation of meniscus, it enables us to fabricate a series of solid solutions based on SECCM. Furthermore, SECCM is an in-situ electrochemical fabrication technique which constructs microcrystals on microchip. Microcrystals constructed on microchip exhibited solid state electrochemical behavior.

Based on SECCM, the electrochemistry of functional microcrystals and behavior of electron transfer on solid/solid interface was investigated. The main contents and results of the thesis are as below.

1. The $\text{Na}_3\text{Co}(\text{CN})_6/\text{NaCl}$ solid solution was constructed on microchip by SECCM. The solid solution exhibited electrochemical reduction of Co(III) which was hard to detect in aqueous solution. The apparent concentration of Co(III) was 9.69×10^{-2} mol/L, the apparent diffusion coefficient of Na^+ ion as counterion in solid solution was 3.89×10^{-8} cm^2/s and apparent electron transfer rate constant was 1.06×10^{-5} cm/s. Because of a small dielectric constant of NaCl, the energy slope of Co(III) reduction in NaCl was much smaller than that in aqueous solution, which was caculated by

density functional theory (DFT). From the perspective of reduction energy slope, it was obvious that reduction of Co(III) in NaCl crystal was more inclined to take place than that in aqueous solution

2. Based on SECCM, iron oxohydroxides/NaCl microcrystals were electrochemically synthesised, the solid microcrystals showed a multiple-step electron transfer behavior. With cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy, it reveals the apparent concentration of iron oxohydroxides was 1.55×10^{-2} mol/L, also the apparent diffusion coefficient of Na^+ ion as counterion in solid solution was $5.36 \times 10^{-10} \text{ cm}^2/\text{s}$ and apparent electron transfer rate constant was $1.29 \times 10^{-4} \text{ cm/s}$. The high mass capacity of solid solution with 625.5 mA h/g indicates its potential application in battery material. The adsorbed water molecules on iron oxohydroxides surface play a crucial role in the electron transfer and mass transfer process. After calcination, the microcrystal turned to a semiconductor and its nonlinear coefficient was 1.92.
3. The $\text{Na}_2\text{IrCl}_6/\text{NaCl}$ solid solution was electrochemically modulated by SECCM. The electrochemical behavior of solid solution was remarkably improved after an electrochemical activation process under a high potential (5V). the behavior of electron transfer in solid solution was electron self-exchange (hopping). The apparent concentration of Ir(IV) was 0.46 mol/L, the apparent diffusion coefficient of Na^+ ion as counterions in solid solution was $4.46 \times 10^{-9} \text{ cm}^2/\text{s}$ and apparent electron transfer rate constant was $1.14 \times 10^{-4} \text{ cm/s}$.

Key words: scanning electrochemical cell microscopy; solid solution; construction; microfabrication; solid/solid interface

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